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Theory of Vibrational Rotational Strengths: Comparison of a Priori Theory and Approximate Models†

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Abstract: The atomic polar tensor (APT), fixed partial charge (FPC), and coupled oscillator (CO) equations for vibrational rotational strengths have been used in the analysis of vibrational circular dichroism (VCD) spectra. The accuracy of these equations is examined by comparison of their predictions for a diverse set of eight, small, chiral molecules to those previously obtained using Stephens' a priori theory of vibrational rotational strengths. The atomic polar and axial tensors central to the latter were evaluated ab initio at the SCF level of approximation, using large basis sets and (in the case of the atomic axial tensors) the distributed origin gauge. Rotational strengths predicted by the APT, FPC, and CO equations are in each case in very poor overall agreement with the predictions of the a priori theory. The causes of the differences are analyzed. The continued use of the APT, FPC, and CO equations is not supported and conclusions arrived at previously resulting from the analysis of VCD spectra using these equations should be reexamined.

Introduction

The theoretical analysis of the vibrational circular dichroism (VCD) spectra of chiral molecules[1,2] requires a theory of vibrational rotational strengths. An a priori theory of vibrational rotational strengths has recently been developed by Stephens[3,4] and implemented[5-23] for a number of molecules at the ab initio SCF level of approximation. In those cases where predictions of VCD spectra have been compared to experiment, encouraging agreement has been obtained.[6,8,11,12,16-18,21-23]

It was recently shown[4] that specific approximations to Stephens' a priori theory lead to three equations for vibrational rotational strengths, identical in form with equations previously advanced: the atomic polar tensor (APT) equation,[24,25] the fixed partial charge (FPC) equation,[26] and the coupled oscillator (CO) equation.[27] These equations have all been used as bases for the interpretation of VCD spectra.[24,28-42] Their relative simplicity is an appealing feature of all three equations. However, the assumptions and approximations on which they have been based can be readily criticized.[1,4] Consequently, the accuracy of these equations is open to question.

Our purpose here is to examine the accuracy of the APT, FPC, and CO equations by comparison of their predictions to those of Stephens' theory. Results obtained[10,11,17,18] using the latter for the molecules NHDT (**1**), hydrazine [NH_2NH_2] (**2**), propane-*1,1,1*-d_3-*2*-d_1 [CH_3CHDCD_3] (**3**), fluorohydroxylamine [NHF(OH)] (**4**), carbodiimide [HN=C=NH] (**5**), *trans*-cyclopropane-*1,2*-d_2 (**6**), *trans*-oxirane-*2,3*-d_2 (**7**), and oxaziridine [CH_2ONH] (**8**) using large basis sets and, hence, of maximal accuracy, form the basis for this comparison.

Theory

Stephens' equation for the rotational strength of the fundamental vibrational transition of the *i*th normal mode, in the distributed origin with origins at nuclei (DO) gauge, is[4]

$$\begin{aligned} R(0\rightarrow 1)_i &= \hbar^2 \mathrm{Im}[\vec{\mathrm{P}}_i \cdot \vec{\mathrm{M}}_i^{\mathrm{DO}}] \\ &= \hbar^2 \mathrm{Im}\left[\vec{P}_i \cdot \left\{\vec{M}_i + \frac{i}{4\hbar c}\vec{L}_i\right\}\right] \\ &= \hbar^2 \mathrm{Im}\left[\vec{P}_i \cdot \vec{M}_i + \left(\frac{i}{4\hbar c}\right)\vec{P}_i \cdot \vec{L}_i\right] \end{aligned} \tag{1}$$

where

$$\mathbf{P}_{i\beta} = \sum_{\lambda} \mathbf{P}^{\lambda}_{i\beta} \qquad \mathbf{P}^{\lambda}_{i\beta} = \sum_{\alpha} \mathbf{P}^{\lambda}_{\alpha\beta}\mathbf{S}_{\lambda\alpha,i}$$

$$(\mathbf{M}_{i\beta})^{\mathrm{DO}} = \sum_{\lambda} (\mathbf{M}^{\lambda}_{i\beta})^{\mathrm{DO}} \qquad (\mathbf{M}^{\lambda}_{i\beta})^{\mathrm{DO}} = \sum_{\alpha} (\mathbf{M}^{\lambda}_{\alpha\beta})^{\mathrm{DO}}\mathbf{S}_{\lambda\alpha,i}$$

$$\mathbf{M}_{i\beta} = \sum_{\lambda} (\mathbf{M}^{\lambda}_{i\beta})^{\lambda} \qquad (\mathbf{M}^{\lambda}_{i\beta})^{\lambda} = \sum_{\alpha} (\mathbf{M}^{\lambda}_{\alpha\beta})^{\lambda}\mathbf{S}_{\lambda\alpha,i}$$

$$\mathbf{L}_{i\beta} = \sum_{\lambda} \mathbf{L}^{\lambda}_{i\beta} \qquad \mathbf{L}^{\lambda}_{i\beta} = \sum_{\alpha} \mathbf{L}^{\lambda}_{\alpha\beta}\mathbf{S}_{\lambda\alpha,i}$$

$$\mathbf{L}^{\lambda}_{\alpha\beta} = \sum_{\gamma,\delta} \epsilon_{\beta\gamma\delta}\mathbf{R}^{0}_{\lambda\gamma}\mathbf{P}^{\lambda}_{\alpha\delta}$$

$$(\mathbf{M}^{\lambda}_{\alpha\beta})^{\mathrm{DO}} = (\mathbf{M}^{\lambda}_{\alpha\beta})^{\lambda} + \frac{i}{4\hbar c}\mathbf{L}^{\lambda}_{\alpha\beta} \tag{2}$$

$\mathbf{P}^{\lambda}_{\alpha\beta}$ and $(\mathbf{M}^{\lambda}_{\alpha\beta})^{\mathrm{DO}}$ are the atomic polar tensor and the DO gauge atomic axial tensor of nucleus λ, respectively.[4] $(\mathbf{M}^{\lambda}_{\alpha\beta})^{\lambda}$ is the

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atomic axial tensor of nucleus λ obtained by using as the origin the equilibrium position of nucleus λ, which is at $\vec{R}_\lambda^0$ from the molecular origin. The $\mathbf{S}_{\lambda\alpha,i}$ matrix determines the transformation of Cartesian displacement coordinates $\mathbf{X}_{\lambda\alpha}$ to normal coordinates $\mathbf{Q}_i$:

$$\mathbf{X}_{\lambda\alpha} = \sum_i \mathbf{S}_{\lambda\alpha,i}\mathbf{Q}_i \tag{3}$$

The corresponding vibrational dipole strength is given by

$$D(0 \rightarrow 1)_i = \left(\frac{\hbar}{2\omega_i}\right)[\vec{P}_i \cdot \vec{P}_i] \tag{4}$$

where ω_i is the frequency of the ith mode. We refer to the first and second terms in eq 1 as the "$\vec{P}\cdot\vec{M}$" and "$\vec{P}\cdot\vec{L}$" terms, respectively.

If $\vec{P}_i\cdot\vec{M}_i$ is zero, then

$$\begin{aligned} R(0 \rightarrow 1)_i &= \frac{\hbar}{4c}\vec{P}_i\cdot\vec{L}_i \\ &= \frac{\hbar}{4c}\sum_{\lambda\lambda'}\vec{P}_i^\lambda\cdot\vec{R}_{\lambda'}^0 \times \vec{P}_i^{\lambda'} = \frac{\hbar}{4c}\sum_{\lambda<\lambda'}\vec{P}_i^\lambda\cdot\vec{R}_{\lambda'\lambda}^0 \times \vec{P}_i^{\lambda'} \end{aligned} \tag{5}$$

where $\vec{R}_{\lambda'\lambda}^0 = \vec{R}_{\lambda'}^0 - \vec{R}_\lambda^0$. Equation 5 is the APT equation.[4] Equations of this form, involving approximate atomic polar tensors, have been derived by Freedman and Nafie, initially[24] as an approximation to the localized molecular orbital equation, and subsequently[25] via the nonlocalized molecular orbital equation.

If the atomic polar tensors $\mathbf{P}_{\alpha\beta}^\lambda$ are of the diagonal form

$$\mathbf{P}_{\alpha\beta}^\lambda = q_\lambda\delta_{\alpha\beta} \tag{6}$$

eq 5 becomes

$$R(0 \rightarrow 1)_i = \frac{\hbar}{4c}\sum_{\lambda<\lambda'} q_\lambda q_{\lambda'}\vec{S}_i^\lambda\cdot\vec{R}_{\lambda'\lambda}^0 \times \vec{S}_i^{\lambda'} \tag{7}$$

where $(\vec{S}_i^\lambda)_\alpha \equiv \mathbf{S}_{\lambda\alpha,i}$. In addition, eq 4 reduces to

$$D(0 \rightarrow 1)_i = \left(\frac{\hbar}{2\omega_i}\right)\sum_{\lambda,\lambda'} q_\lambda q_{\lambda'}\vec{S}_i^\lambda\cdot\vec{S}_i^{\lambda'} \tag{8}$$

Equation 7 is identical in form to the FPC equation, given by Schellman.[26]

When two modes, designated + and −, exist such that

$$\vec{P}_\pm = \vec{P}_\mathrm{A} \pm \vec{P}_\mathrm{B} \tag{9}$$

where A and B are localized groups of atoms, and with the approximation that

$$\vec{R}_{\lambda_\mathrm{B}\lambda_\mathrm{A}}^0 \approx \vec{R}_\mathrm{BA}^0 = (\vec{R}_\mathrm{B}^0 - \vec{R}_\mathrm{A}^0) \tag{10}$$

eqs 4 and 5 reduce to

$$D(0 \rightarrow 1)_\pm = \left(\frac{\hbar}{2\omega_\pm}\right)[(\vec{P}_\mathrm{A} \pm \vec{P}_\mathrm{B})\cdot(\vec{P}_\mathrm{A} \pm \vec{P}_\mathrm{B})] \tag{11}$$

$$R(0 \rightarrow 1)_\pm = \pm\frac{\hbar}{4c}\vec{P}_\mathrm{A}\cdot\vec{R}_\mathrm{BA}^0 \times \vec{P}_\mathrm{B} \tag{12}$$ [49]

Further approximating $\omega_\pm \approx \omega$, we can write

$$D(0 \rightarrow 1)_\pm = |\vec{\mu}_\pm|^2 \tag{13}$$

$$\vec{\mu}_\pm = \vec{\mu}_\mathrm{A} \pm \vec{\mu}_\mathrm{B}$$

$$\vec{\mu}_\mathrm{A} = \left(\frac{\hbar}{2\omega}\right)^{1/2}\vec{P}_\mathrm{A} \qquad \vec{\mu}_\mathrm{B} = \left(\frac{\hbar}{2\omega}\right)^{1/2}\vec{P}_\mathrm{B}$$

whence

$$R(0 \rightarrow 1)_\pm = \pm\left(\frac{\omega}{2c}\right)\vec{\mu}_\mathrm{A}\cdot\vec{R}_\mathrm{BA}^0 \times \vec{\mu}_\mathrm{B} \tag{14}$$ [49]

Equation 14 possesses the form of the CO equation, derived by Holzwarth and Chabay.[27]

Methods

The tensors $\mathbf{P}_{\alpha\beta}^\lambda$, $(\mathbf{M}_{\alpha\beta}^\lambda)^\mathrm{DO}$, $(\mathbf{M}_{\alpha\beta}^\lambda)^\lambda$, and $\mathbf{L}_{\alpha\beta}^\lambda$ were calculated previously[10,11,17,18] for molecules **1**–**8** for a variety of basis sets using analytical derivative methods and the CADPAC program.[7] Here, we use the most accurate of the results. In the case of NHDT[10] and NH_2NH_2[17] these were obtained using the (13s8p3d/10s3p) − [8s6p3d/6s3p] VD/3P basis set. In other cases,[11,17,18] these were obtained using the (11s5p2d/5s2p) − [4s3p2d/3s2p] 6-31G(ext) basis set. D and R values for **1**–**8** were calculated previously from these tensors using eqs 1 and 4 and specific choices of equilibrium geometry and force field. With the exception of **1**, **6**, and **7**, these were calculated ab initio at the SCF level of approximation using the 3-21G basis set.[17] For **1** and **6** experimental geometries and empirical force fields were used.[10,17] For **7** the experimental geometry and a scaled ab initio SCF 6-31G-(ext) force field were used.[11,18]

The predictions of the APT equation (eq 5) are obtained by suppressing the "$\vec{P}\cdot\vec{M}$" term of eq 1. Dipole strengths are unaffected.

In order to examine the FPC equation (eq 7) q_λ values are required. We obtain these in two ways. First, q_λ is put equal to the average of the diagonal elements of the calculated $\mathbf{P}_{\alpha\beta}^\lambda$ tensors:[50]

$$q_\lambda = \tfrac{1}{3}\sum_\alpha \mathbf{P}_{\alpha\alpha}^\lambda \tag{15}$$

(Note that the automatic satisfaction of the sum rule for a neutral molecule, $\sum_\lambda \mathbf{P}_{\alpha\beta}^\lambda = 0$, when $\mathbf{P}_{\alpha\beta}^\lambda$ tensors are calculated with analytical derivative methods,[15,17] guarantees that $\sum_\lambda q_\lambda = 0$, a necessary constraint in any choice of q_λ values.) Second, q_λ is equated to the atomic charge obtained by using Mulliken population analysis (MPA) of the SCF wave function for the same basis set as used in calculating $\mathbf{P}_{\alpha\beta}^\lambda$ tensors. D and R values are then obtained using the same equilibrium geometries and force fields as employed in the calculations using eqs 1 and 4.

The CO equation is examined in those molecules possessing C_2 symmetry (**2**, **5**, **6**, and **7**) and for those modes to which its application is most likely to be efficacious. These comprise the NH_2 symmetric and antisymmetric stretching modes of **2**, the NH stretching modes of **5**, the CD stretching modes of **6**, and the C–H and C–D stretching modes of **7**. Following identification of the + and − modes corresponding to these chromophores, $\vec{\mu}_\mathrm{A}$ and $\vec{\mu}_\mathrm{B}$ vectors are obtained from the calculated $\vec{\mu}_+$ and $\vec{\mu}_-$ vectors via eq 13. The frequency ω is $^1/_2(\omega_+ + \omega_-)$. The choice of the vectors

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Table I. Atomic Polar and Axial Tensors for NHDT (**1**)[a-d]

			$P^{\lambda}_{\alpha\beta}$						$M^{\lambda}_{\alpha\beta}$	
λ	α	β	e	FPC/APT[f]	FPC/MPA[g]	$M^{\lambda}_{\alpha\beta}$[e]	$(M^{\lambda}_{\alpha\beta})^{\lambda}$[e]	$(i/4\hbar c)L^{\lambda}_{\alpha\beta}$[e]	FPC/APT[h]	FPC/MPA[i]
N_1	X	X	−0.376	−0.447	−0.649	0.000	0.000	0.000	0.000	0.000
	X	Y	0.000	0.000	0.000	0.086	0.099	−0.012	−0.014	−0.021
	X	Z	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Y	X	0.000	0.000	0.000	−0.086	−0.099	0.012	0.014	0.021
	Y	Y	−0.376	−0.447	−0.649	0.000	0.000	0.000	0.000	0.000
	Y	Z	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	X	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Y	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Z	−0.590	−0.447	−0.649	0.000	0.000	0.000	0.000	0.000
H_2	X	X	0.144	0.149	0.216	−0.005	0.010	−0.015	0.000	0.000
	X	Y	0.032	0.000	0.000	−0.078	−0.046	−0.033	−0.022	−0.032
	X	Z	−0.051	0.000	0.000	−0.192	−0.129	−0.062	−0.057	−0.083
	Y	X	0.032	0.000	0.000	0.083	0.034	0.049	0.022	0.032
	Y	Y	0.107	0.149	0.216	0.005	−0.010	0.015	0.000	0.000
	Y	Z	0.088	0.000	0.000	−0.111	−0.075	−0.036	−0.033	−0.048
	Z	X	−0.069	0.000	0.000	0.228	0.135	0.093	0.057	0.083
	Z	Y	0.119	0.000	0.000	0.132	0.078	0.054	0.033	0.048
	Z	Z	0.197	0.149	0.216	0.000	0.000	0.000	0.000	0.000

[a] Cartesian geometry (atomic units): N_1(0.00000, 0.000000, 0.127811), H_2(−0.885499, 1.533729, −0.591952), D_3(−0.885499, −1.533729, −0.591952), and T_4(1.770998, 0.00000, −0.591952). Origin is at the center of mass of NH_3. Geometry is experimental geometry of NH_3 from J. L. Duncan and I. M. Mills [*Spectrochim. Acta* **1964**, *20*, 523]: $r_{NH} = 1.0116$ Å and $\theta_{HNH} = 106.7°$. [b] All ab initio calculations using VD/3P basis set.[9,10,13,15] [c] $P^{\lambda}_{\alpha\beta}$ and $M^{\lambda}_{\alpha\beta}$ tensors in atomic units.[9,15] $\mathrm{Im}[M^{\lambda}_{\alpha\beta}]$ is given. [d] Origin for atomic axial tensors is the center of mass of NH_3. [e] Ab initio values. [f] Calculated using eqs 6 and 15. $q_N = -0.447$, $q_H = q_D = q_T = 0.149$ au. [g] Calculated using eq 6; q_{λ} obtained via Mulliken population analysis. $q_N = -0.649$, $q_H = q_D = q_T = 0.216$ au. [h] Calculated using eq 18. q_{λ} obtained from eq 15. [i] Calculated using eq 18. q_{λ} obtained via Mulliken population analysis.

Table II. Atomic Polar and Axial Tensors for Hydrazine, NH_2NH_2 (**2**)[a-c]

			$P^{\lambda}_{\alpha\beta}$						$M^{\lambda}_{\alpha\beta}$	
λ	α	β		FPC/APT[d]	FPC/MPA[e]	$M^{\lambda}_{\alpha\beta}$	$(M^{\lambda}_{\alpha\beta})^{\lambda}$	$(i/4\hbar c)L^{\lambda}_{\alpha\beta}$	FPC/APT[d]	FPC/MPA[e]
N_1	X	X	−0.335	−0.268	−0.438	−0.129	−0.071	−0.058	0.000	0.000
	X	Y	0.137	0.000	0.000	−0.024	−0.030	0.006	0.005	0.007
	X	Z	0.176	0.000	0.000	−0.561	−0.446	−0.115	−0.092	−0.150
	Y	X	0.074	0.000	0.000	0.063	0.030	0.033	−0.005	−0.007
	Y	Y	−0.159	−0.268	−0.438	0.000	0.001	−0.001	0.000	0.000
	Y	Z	−0.103	0.000	0.000	0.095	0.070	0.025	0.000	0.000
	Z	X	0.180	0.000	0.000	0.498	0.392	0.106	0.092	0.150
	Z	Y	0.021	0.000	0.000	−0.077	−0.074	−0.003	0.000	0.000
	Z	Z	−0.309	−0.268	−0.438	0.143	0.081	0.062	0.000	0.000
H_3	X	X	0.086	0.149	0.234	0.059	0.049	0.010	0.000	0.000
	X	Y	−0.072	0.000	0.000	−0.114	−0.081	−0.033	−0.025	−0.039
	X	Z	−0.044	0.000	0.000	−0.013	−0.085	0.073	0.074	0.116
	Y	X	−0.020	0.000	0.000	0.063	0.071	−0.007	0.025	0.039
	Y	Y	0.111	0.149	0.234	0.021	−0.004	0.025	0.000	0.000
	Y	Z	0.052	0.000	0.000	−0.198	−0.141	−0.057	−0.063	−0.099
	Z	X	−0.026	0.000	0.000	−0.120	−0.006	−0.114	−0.074	−0.116
	Z	Y	0.064	0.000	0.000	0.236	0.126	0.110	0.063	0.099
	Z	Z	0.251	0.149	0.234	−0.072	−0.032	−0.040	0.000	0.000
H_5	X	X	0.250	0.118	0.204	0.069	0.023	0.046	0.000	0.000
	X	Y	−0.065	0.000	0.000	0.223	0.118	0.105	0.048	0.082
	X	Z	−0.038	0.000	0.000	0.136	0.012	0.125	0.063	0.108
	Y	X	−0.054	0.000	0.000	−0.217	−0.180	−0.036	−0.048	−0.082
	Y	Y	0.048	0.118	0.204	−0.022	0.003	−0.025	0.000	0.000
	Y	Z	0.032	0.000	0.000	0.048	0.071	−0.023	0.014	0.024
	Z	X	−0.055	0.000	0.000	0.039	0.104	−0.065	−0.063	−0.108
	Z	Y	0.085	0.000	0.000	−0.085	−0.055	−0.029	−0.014	−0.024
	Z	Z	0.058	0.118	0.204	−0.071	−0.052	−0.019	0.000	0.000

[a] Cartesian geometry (atomic units): N_1(0.000000, −1.369629, −0.067720), N_2(0.000000, 1.369629, −0.067720), H_3(−1.684722, −1.990381, −0.670110), H_4(1.684722, 1.990381, −0.670110), H_5(0.474973, −2.124884, 1.611036), and H_6(−0.474973, 2.124884, 1.611036). Origin is at center of mass of NH_2NH_2. Geometry is 3-21G SCF geometry:[17] $r_{N_1H_3} = r_{N_2H_4} = 1.002$ Å, $r_{N_1H_5} = r_{N_2H_6} = 1.006$ Å, $r_{N_1N_2} = 1.450$ Å, $\theta_{H_3N_1N_2} = 109.13°$, $\theta_{H_5N_1N_2} = 113.41°$, $\theta_{H_3N_1H_5} = 111.90°$, $\tau_{H_3N_1N_2H_6} = \tau_{H_5N_1N_2H_4} = -93.88°$. [b] All ab initio calculations using the VD/3P basis set.[17] [c] Notation and units as in Table I. Origin for atomic axial tensors is the center of mass of NH_2NH_2. [d] $q_N = -0.268$, $q_{H_3} = 0.149$, $q_{H_5} = 0.118$ au. [e] $q_N = -0.438$, $q_{H_3} = 0.234$, $q_{H_5} = 0.204$ au.

$\vec{R}_{BA}$ is not uniquely defined and we therefore employ a selection of "reasonable" choices.

In conjunction with the CO equation a dipole–dipole approximation to the splitting of the + and − modes is often adopted, in which

$$\omega_+ - \omega_- = 2[(\vec{\mu}_A \cdot \vec{\mu}_B)/|\vec{R}_{BA}|^3 - 3(\vec{\mu}_A \cdot \vec{R}_{AB})(\vec{\mu}_B \cdot \vec{R}_{AB})/|\vec{R}_{BA}|^5] \tag{16}$$

We also calculate $\omega_+ - \omega_-$ values via eq 16.

Results and Discussion

The $P^{\lambda}_{\alpha\beta}$, $(M^{\lambda}_{\alpha\beta})^{DO}$, $(M^{\lambda}_{\alpha\beta})^{\lambda}$, and $(i/4\hbar c)L^{\lambda}_{\alpha\beta}$ tensors obtained previously for **1**–**8**[10,11,17,18] are given in Tables I–VIII. The enantiomer, equilibrium geometry, origin, and basis set used for each molecule are also specified in Tables I–VIII. The *D* and *R* values derived thence are given in Tables IX–XVI. The contributions of the "$\vec{P}\cdot\vec{M}$" and "$\vec{P}\cdot\vec{L}$" terms to the *R* values are also given separately in Tables IX–XVI. As discussed previously,[10,11,17,18] the results given in Tables I–XVI are good approximations to Hartree–Fock limiting values. In the cases of

Table III. Atomic and Axial Tensors for Propane-*1,1,1*-d_3-*2*-d_1, CH_3CHDCD_3 (3)[a-c]

			$P_{\alpha\beta}^{\lambda}$						$M_{\alpha\beta}^{\lambda}$	
λ	α	β		FPC/APT[d]	FPC/MPA[e]	$M_{\alpha\beta}^{\lambda}$	$(M_{\alpha\beta}^{\lambda})^{\lambda}$	$(i/4\hbar c)L_{\alpha\beta}^{\lambda}$	FPC/APT[d]	FPC/MPA[e]
C_1	X	X	0.191	0.172	−0.421	0.000	0.000	0.000	0.000	0.000
	X	Y	0.000	0.000	0.000	−0.097	−0.150	0.053	0.048	−0.117
	X	Z	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Y	X	0.000	0.000	0.000	0.115	0.162	−0.047	−0.048	0.117
	Y	Y	0.168	0.172	−0.421	0.000	0.000	0.000	0.000	0.000
	Y	Z	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	X	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Y	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Z	0.158	0.172	−0.421	0.000	0.000	0.000	0.000	0.000
C_2	X	X	0.168	0.113	−0.823	0.000	0.000	0.000	0.000	0.000
	X	Y	0.000	0.000	0.000	0.064	0.086	−0.022	−0.015	0.107
	X	Z	0.000	0.000	0.000	−0.064	−0.165	0.101	0.068	−0.496
	Y	X	0.000	0.000	0.000	−0.019	−0.055	0.036	0.015	−0.107
	Y	Y	0.057	0.113	−0.823	0.000	0.000	0.000	0.000	0.000
	Y	Z	−0.047	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	X	0.000	0.000	0.000	0.059	0.132	−0.073	−0.068	0.496
	Z	Y	−0.033	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Z	0.114	0.113	−0.823	0.000	0.000	0.000	0.000	0.000
H_4	X	X	−0.108	−0.068	0.251	0.000	0.000	0.000	0.000	0.000
	X	Y	0.000	0.000	0.000	−0.061	−0.057	−0.004	−0.040	0.146
	X	Z	0.145	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Y	X	0.000	0.000	0.000	−0.045	−0.058	0.012	0.040	−0.146
	Y	Y	−0.021	−0.068	0.251	0.000	0.000	0.000	0.000	0.000
	Y	Z	0.000	0.000	0.000	−0.108	−0.116	0.009	0.028	−0.103
	Z	X	0.112	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Y	0.000	0.000	0.000	0.134	0.099	0.035	−0.028	0.103
	Z	Z	−0.075	−0.068	0.251	0.000	0.000	0.000	0.000	0.000
H_6	X	X	0.062	−0.047	0.246	0.000	0.000	0.000	0.000	0.000
	X	Y	0.000	0.000	0.000	0.075	0.065	0.010	−0.008	0.040
	X	Z	0.000	0.000	0.000	0.099	0.036	0.064	−0.048	0.251
	Y	X	0.000	0.000	0.000	−0.192	−0.135	−0.056	0.008	−0.040
	Y	Y	−0.172	−0.047	0.246	0.000	0.000	0.000	0.000	0.000
	Y	Z	0.082	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	X	0.000	0.000	0.000	−0.001	−0.014	0.013	0.048	−0.251
	Z	Y	0.117	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Z	−0.032	−0.047	0.246	0.000	0.000	0.000	0.000	0.000
H_8	X	X	−0.108	−0.042	0.268	0.090	0.022	0.069	0.000	0.000
	X	Y	−0.020	0.000	0.000	−0.013	−0.007	−0.005	0.018	−0.115
	X	Z	−0.125	0.000	0.000	−0.117	−0.059	−0.059	−0.026	0.165
	Y	X	0.023	0.000	0.000	0.097	0.083	0.014	−0.018	0.115
	Y	Y	0.026	−0.042	0.268	0.001	0.012	−0.012	0.000	0.000
	Y	Z	−0.004	0.000	0.000	−0.118	−0.121	0.003	0.017	−0.111
	Z	X	−0.105	0.000	0.000	0.056	0.047	0.009	0.026	−0.165
	Z	Y	−0.040	0.000	0.000	0.127	0.100	0.027	−0.017	0.111
	Z	Z	−0.043	−0.042	0.268	−0.087	−0.039	−0.048	0.000	0.000

[a] Cartesian geometry (atomic units): C_1(0.000000, 0.000000, 1.114746), C_2(0.000000, −2.410244, −0.518807), C_3(0.000000, 2.410244, −0.518807), D_4(−1.650352, 0.000000, 2.331251), H_5(1.650352, 0.000000, 2.331251), H_6(0.000000, −4.093451, 0.650275), D_7(0.000000), 4.093451, 0.650275), H_8(−1.660469, −2.464370, −1.720361), D_9(−1.660469, 2.464370, −1.720361), H_{10}(1.660469, −2.464370, −1.720361), and D_{11}(1.660469, 2.464370, −1.720361). Origin is at center of mass of $CH_3CH_2CH_3$. Geometry is 3-21G SCF geometry:[17] $r_{C_1C_2} = r_{C_1C_3} = 1.541$ Å, $r_{C_1D_4} = r_{C_1H_5} = 1.085$ Å, $r_{C_2H_6} = r_{C_3D_7} = 1.084$ Å, $r_{C_2H_8} = r_{C_2H_{10}} = r_{C_3D_9} = r_{C_3D_{11}} = 1.085$ Å, $\theta_{D_4C_1H_5} = 107.21°$, $\theta_{C_2C_1C_3} = 111.74°$, $\theta_{H_6C_2H_8} = \theta_{D_7C_3D_{11}} = 108.22° = \theta_{H_6C_2H_{10}} = \theta_{D_7C_3D_9}$, $\theta_{H_8C_2H_{10}} = \theta_{D_{11}C_3D_9} = 108.16°$, $\theta_{D_4C_1C_3} = \theta_{H_5C_1C_2} = 109.44°$, $\theta_{H_6C_2C_1} = \theta_{D_7C_3C_1} = 111.09°$, and $\theta_{D_9C_3C_1} = \theta_{D_{11}C_3C_1} = \theta_{H_8C_2C_1} = \theta_{H_{10}C_2C_1} = 110.53°$. [b] All ab initio calculations with the 6-31G(ext) basis set.[17] [c] Notation and units as in Table I. Origin for all atomic axial tensors is center of mass of $CH_3CH_2CH_3$. [d] $q_{C_1} = 0.172$, $q_{C_2} = 0.113$. $q_{H_4} = -0.068$, $q_{H_6} = -0.047$, and $q_{H_8} = -0.042$ au. [e] $q_{C_1} = -0.421$, $q_{C_2} = -0.823$, $q_{H_4} = 0.251$, $q_{H_6} = 0.246$, and $q_{H_8} = 0.268$ au.

6 and **7** calculated VCD spectra predicted from rotational strengths have been compared to experimental VCD spectra;[11,17,18] agreement was excellent.

In the APT equation (eq 5) the "$\vec{P}\cdot\vec{L}$" term of eq 1 is present and the "$\vec{P}\cdot\vec{M}$" term is missing. This is tantamount to the assumption, for all λ, that

$$(M_{\alpha\beta}^{\lambda})^{DO} = \left(\frac{i}{4\hbar c}\right)L_{\alpha\beta}^{\lambda};\ (M_{\alpha\beta}^{\lambda})^{\lambda} = 0 \qquad (17)$$

Examination of Tables I–XVI shows that in general the contributions of $(M_{\alpha\beta}^{\lambda})^{\lambda}$ tensors to $(M_{\alpha\beta}^{\lambda})^{DO}$ tensors and the contributions of the "$\vec{P}\cdot\vec{M}$" terms to *R* values are both substantial. In examining the relative contributions of $(M_{\alpha\beta}^{\lambda})^{\lambda}$ and $(i/4\hbar c)L_{\alpha\beta}^{\lambda}$ tensors to $(M_{\alpha\beta}^{\lambda})^{DO}$ tensors it must be remembered that $(M_{\alpha\beta}^{\lambda})^{\lambda}$ is origin-independent while $(i/4\hbar c)L_{\alpha\beta}^{\lambda}$ is dependent on the choice of origin. The relative magnitudes of $(M_{\alpha\beta}^{\lambda})^{\lambda}$ and $(i/4\hbar c)L_{\alpha\beta}^{\lambda}$ contributions to $(M_{\alpha\beta}^{\lambda})^{DO}$ tensors are thus origin-dependent. However, the "$\vec{P}\cdot\vec{M}$" and "$\vec{P}\cdot\vec{L}$" contributions to *R* values are both origin-independent and the relative magnitudes of the "$\vec{P}\cdot\vec{M}$" and "$\vec{P}\cdot\vec{L}$" terms, given in Tables IX–XVI, are not affected by a change in origin.

It is clear that the $(M_{\alpha\beta}^{\lambda})^{\lambda}$ contributions to $(M_{\alpha\beta}^{\lambda})^{DO}$ tensors and the "$\vec{P}\cdot\vec{M}$" contributions to *R* values are not negligible. In fact, in the majority of cases, the contributions of the "$\vec{P}\cdot\vec{M}$" terms to *R* values are larger than the contributions of the "$\vec{P}\cdot\vec{L}$" terms. The APT equation thus *generally* leads to very inaccurate results. Of course, in some specific instances the "$\vec{P}\cdot\vec{L}$" terms dominate the "$\vec{P}\cdot\vec{M}$" terms, but statistically this is infrequent.

The FPC equation derives from the APT equation on replacement of the atomic polar tensors $P_{\alpha\beta}^{\lambda}$ by constant diagonal tensors $q_\lambda\delta_{\alpha\beta}$. The q_λ parameters are the "fixed partial charges". If $P_{\alpha\beta}^{\lambda} = q_\lambda\delta_{\alpha\beta}$, $L_{\alpha\beta}^{\lambda}$ and $(M_{\alpha\beta}^{\lambda})^{DO}$ reduce to

$$L_{\alpha\beta}^{\lambda} = q_\lambda\sum_{\gamma}\epsilon_{\alpha\beta\gamma}R_{\lambda\gamma}^{0} \qquad (M_{\alpha\beta}^{\lambda})^{DO} = \frac{i}{4\hbar c}q_\lambda\sum_{\gamma}\epsilon_{\alpha\beta\gamma}R_{\lambda\gamma}^{0} \qquad (18)$$

The results given in Tables I–VIII show that in general this

Table IV. Atomic Polar and Axial Tensors for Fluorohydroxylamine, NHF(OH) (4)[a-c]

γ	α	β	$P^{\lambda}_{\alpha\beta}$			$M^{\lambda}_{\alpha\beta}$	$(M^{\lambda}_{\alpha\beta})^{\lambda}$	$(i/4\hbar c)L^{\lambda}_{\alpha\beta}$	$M^{\lambda}_{\alpha\beta}$	
				FPC/APT[d]	FPC/MPA[e]				FPC/APT[d]	FPC/MPA[e]
N_1	X	X	0.110	0.539	0.398	−0.135	−0.072	−0.063	0.000	0.000
	X	Y	−0.216	0.000	0.000	0.243	0.268	−0.025	−0.086	−0.064
	X	Z	0.121	0.000	0.000	−0.397	−0.410	0.013	0.127	0.094
	Y	X	−0.125	0.000	0.000	0.061	−0.173	0.233	0.086	0.064
	Y	Y	0.814	0.539	0.398	0.024	−0.022	0.046	0.000	0.000
	Y	Z	−0.437	0.000	0.000	−0.120	−0.139	0.019	0.032	0.024
	Z	X	0.127	0.000	0.000	−0.062	0.166	−0.228	−0.127	−0.094
	Z	Y	−0.405	0.000	0.000	0.009	0.071	−0.062	−0.032	−0.024
	Z	Z	0.693	0.539	0.398	0.022	0.016	0.006	0.000	0.000
O_2	X	X	−0.256	−0.496	−0.564	−0.031	−0.013	−0.018	0.000	0.000
	X	Y	0.042	0.000	0.000	−0.491	−0.359	−0.132	−0.257	−0.293
	X	Z	−0.014	0.000	0.000	−0.048	0.011	−0.059	−0.117	−0.134
	Y	X	0.029	0.000	0.000	0.811	0.570	0.242	0.257	0.293
	Y	Y	−0.426	−0.496	−0.564	0.064	0.046	0.018	0.000	0.000
	Y	Z	−0.087	0.000	0.000	−0.023	−0.015	−0.008	−0.017	−0.020
	Z	X	−0.130	0.000	0.000	0.406	0.312	0.094	0.117	0.134
	Z	Y	0.187	0.000	0.000	0.235	0.275	−0.040	0.017	0.020
	Z	Z	−0.805	−0.496	−0.564	−0.020	0.005	−0.024	0.000	0.000
H_3	X	X	0.266	0.306	0.388	−0.006	−0.021	0.015	0.000	0.000
	X	Y	−0.040	0.000	0.000	0.115	−0.025	0.140	0.199	0.252
	X	Z	0.072	0.000	0.000	0.024	0.002	0.022	0.046	0.058
	Y	X	−0.029	0.000	0.000	−0.301	−0.073	−0.228	−0.199	−0.252
	Y	Y	0.347	0.306	0.388	−0.033	−0.006	−0.027	0.000	0.000
	Y	Z	0.018	0.000	0.000	0.282	0.125	0.157	0.142	0.180
	Z	X	0.039	0.000	0.000	−0.024	0.029	−0.053	−0.046	−0.058
	Z	Y	0.010	0.000	0.000	−0.285	−0.168	−0.117	−0.142	−0.180
	Z	Z	0.306	0.306	0.388	0.018	0.008	0.011	0.000	0.000
H_4	X	X	0.146	0.182	0.315	−0.003	−0.010	0.007	0.000	0.000
	X	Y	−0.033	0.000	0.000	−0.025	0.027	−0.052	−0.050	−0.086
	X	Z	−0.036	0.000	0.000	0.040	−0.038	0.078	0.083	0.142
	Y	X	0.021	0.000	0.000	0.064	0.039	0.025	0.050	0.086
	Y	Y	0.196	0.182	0.315	0.061	0.044	0.016	0.000	0.000
	Y	Z	0.063	0.000	0.000	−0.022	0.038	−0.059	−0.064	−0.110
	Z	X	0.006	0.000	0.000	−0.122	−0.045	−0.077	−0.083	−0.142
	Z	Y	0.057	0.000	0.000	0.103	0.033	0.070	0.064	0.110
	Z	Z	0.205	0.182	0.315	−0.053	−0.036	−0.017	0.000	0.000
F_5	X	X	−0.266	−0.532	−0.537	0.176	0.150	0.026	0.000	0.000
	X	Y	0.248	0.000	0.000	0.209	0.130	0.079	0.180	0.182
	X	Z	−0.143	0.000	0.000	0.532	0.444	0.088	0.216	0.218
	Y	X	0.104	0.000	0.000	−0.685	−0.549	−0.136	−0.180	−0.182
	Y	Y	−0.931	−0.532	−0.537	−0.115	−0.115	0.000	0.000	0.000
	Y	Z	0.442	0.000	0.000	−0.079	−0.111	0.032	0.042	0.043
	Z	X	−0.042	0.000	0.000	−0.343	−0.233	−0.111	−0.216	−0.218
	Z	Y	0.151	0.000	0.000	−0.094	−0.077	−0.017	−0.042	−0.043
	Z	Z	−0.399	−0.532	−0.537	0.031	0.026	0.005	0.000	0.000

[a] Cartesian geometry (in atomic units): N_1(0.239921, −0.944469, −0.639945), O_2(0.138704, −0.947016, 2.074875), H_3(1.857316, −0.602945, 2.602426), H_4(−1.401961, −1.809124, −1.086799), and F_5(−0.317770, 1.621392, −1.355574). Origin is at center of mass of NHF(OH). Geometry is 3-21G SCF geometry:[17] $r_{N_1O_2} = 1.438$ Å, $r_{N_1H_4} = 1.010$ Å, $r_{N_1F_5} = 1.440$ Å, $r_{O_2H_3} = 0.969$ Å, $\theta_{F_5N_1H_4} = 100.91°$, $\theta_{F_5N_1O_2} = 104.83°$, $\theta_{H_4N_1O_2} = 101.62°$, $\theta_{N_1O_2H_3} = 104.65°$, $\tau_{H_4N_1O_2H_3} = -163.66°$ and $\tau_{F_5N_1O_2H_3} = 91.61°$. [b] All ab initio calculations using the 6-31G(ext) basis set.[17] [c] Notation and units as in Table I. Origin for all atomic axial tensors is center of mass of NHF(OH). [d] $q_{N_1} = 0.539$, $q_{O_2} = -0.496$, $q_{H_3} = 0.306$, $q_{H_4} = 0.182$, and $q_{F_5} = -0.532$ au. [e] $q_{N_1} = 0.398$, $q_{O_2} = -0.564$, $q_{H_3} = 0.388$, $q_{H_4} = 0.315$, and $q_{F_5} = -0.537$ au.

approximation is not at all accurate for either choice of charges. It follows that the FPC equation must provide *R* values in poor agreement with those obtained from the APT equation. The calculated *R* values given in Tables IX–XVI bear out this conclusion. Since the APT equation itself inadequately represents rotational strengths, as discussed above, it follows that the FPC equation is an approximation doubly lacking in accuracy.

The procedure for choosing the q_{λ} parameters in any implementation of the FPC equation is arbitrary. Our results for two different (yet equally reasonable) procedures differ appreciably, showing that the results are not only inaccurate but also poorly defined.

In deriving the APT equation no approximation to $P^{\lambda}_{\alpha\beta}$ tensors was invoked and consequently *D* values were not simultaneously approximated. The further approximation leading to the FPC equation degrades the accuracy of *D* values also. The results of Tables IX–XVI show that the loss of accuracy is very substantial, further emphasizing the inadequacy of the approximation on which the FPC equation is based.

We turn now to the CO equation (eq 14). This constitutes a different approximation to the APT equation. The predictions of the CO equation for selected modes of **2**, **5**, **6**, and **7** are given in Tables X, XIII, XIV, and XV, in each case with several choices of $\vec{R}_{BA}$. The results follow the results of the APT equation qualitatively. Quantitatively, the agreement depends on the choice of the $\vec{R}_{BA}$ vector. Since the APT equation is itself a poor approximation, the results of the CO equation are necessarily also poor.

Splittings of the (+) and (−) modes calculated with eq 16 are given in Table XVII and compared to those predicted by our force fields. The predictions of eq 16 are overall very bad, both in sign and in magnitude.

The systematic derivation of the APT, FPC, and CO equations by stepwise approximations to Stephens' theory was described previously.[4] However, the quantitative accuracy of the approximations involved was not discussed. The results given here comprise the first thorough quantitative examination of the accuracy of the APT, FPC, and CO equations. Our general conclusions are that the APT equation does not accurately predict rotational strengths and that the FPC and CO equations, which further approximate the APT equation, are significantly lower in accuracy still. In addition, the undefined parameters of the

Table V. Atomic Polar and Axial Tensors for Carbodiimide, HN═C═NH (**5**)[a-c]

			$P^\lambda_{\alpha\beta}$						$M^\lambda_{\alpha\beta}$	
λ	α	β		FPC/APT[d]	FPC/MPA[e]	$M^\lambda_{\alpha\beta}$	$(M^\lambda_{\alpha\beta})^\lambda$	$(i/4\hbar c)L^\lambda_{\alpha\beta}$	FPC/APT[d]	FPC/MPA[e]
C_1	X	X	0.340	1.375	0.208	−0.028	−0.030	0.001	0.000	0.000
	X	Y	−0.123	0.000	0.000	−0.017	−0.021	0.004	0.015	0.002
	X	Z	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Y	X	0.052	0.000	0.000	0.207	0.245	−0.038	−0.015	−0.002
	Y	Y	3.455	1.375	0.208	0.000	−0.001	0.001	0.000	0.000
	Y	Z	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	X	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Y	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Z	0.330	1.375	0.208	0.017	0.017	0.000	0.000	0.000
N_2	X	X	−0.478	−1.061	−0.420	0.030	−0.013	0.043	0.000	0.000
	X	Y	0.131	0.000	0.000	0.049	0.040	0.010	0.022	0.009
	X	Z	−0.070	0.000	0.000	−0.662	−0.391	−0.271	−0.602	−0.238
	Y	X	−0.043	0.000	0.000	−0.026	0.034	−0.061	−0.022	−0.009
	Y	Y	−2.250	−1.061	−0.420	−0.007	−0.008	0.001	0.000	0.000
	Y	Z	0.025	0.000	0.000	−0.019	0.006	−0.024	0.000	0.000
	Z	X	−0.121	0.000	0.000	0.689	0.436	0.254	0.602	0.238
	Z	Y	−0.252	0.000	0.000	0.047	0.044	0.002	0.000	0.000
	Z	Z	−0.456	−1.061	−0.420	0.000	0.069	−0.069	0.000	0.000
H_4	X	X	0.308	0.374	0.316	−0.023	0.001	−0.023	0.000	0.000
	X	Y	−0.069	0.000	0.000	0.058	−0.021	0.079	0.082	0.069
	X	Z	0.044	0.000	0.000	0.322	0.035	0.288	0.327	0.276
	Y	X	0.017	0.000	0.000	−0.161	−0.050	−0.111	−0.082	−0.069
	Y	Y	0.523	0.374	0.316	0.006	0.003	0.002	0.000	0.000
	Y	Z	−0.005	0.000	0.000	−0.186	−0.062	−0.124	−0.099	−0.083
	Z	X	0.073	0.000	0.000	−0.348	−0.078	−0.270	−0.327	−0.276
	Z	Y	0.070	0.000	0.000	0.079	−0.014	0.093	0.099	0.083
	Z	Z	0.291	0.374	0.316	−0.019	−0.065	0.045	0.000	0.000

[a] Cartesian geometry (in atomic units): C_1(0.000000, 0.000000, 0.044370), N_2(0.000000, −2.269441, −0.082265), N_3(0.000000, 2.269441, −0.082265), H_4(−1.058469, −3.499986, 0.878865), and H_5(1.058469, 3.499986, 0.878865). Origin is center of mass of HN═C═NH. Geometry is 3-21G SCF geometry:[17] $r_{C_1N_2} = r_{C_1N_3} = 1.203$ Å, $r_{N_2H_4} = r_{N_3H_5} = 0.998$ Å, $\theta_{H_5N_3C_1} = \theta_{H_4N_2C_1} = 128.53°$, $\theta_{N_3C_1N_2} = 173.61°$, and $\tau_{H_4N_2C_1N_3} = \tau_{H_5N_3C_1N_2} = -134.17°$. [b] All ab initio calculations using the 6-31G(ext) basis set.[17] [c] Notation and units as in Table I. Origin for all atomic axial tensors is center of mass of HN═C═NH. [d] $q_{C_1} = 1.375$, $q_{N_2} = -1.061$, and $q_{H_4} = 0.374$ au. [e] $q_{C_1} = 0.208$, $q_{N_2} = -0.420$, and $q_{H_4} = 0.316$ au.

Table VI. Atomic Polar and Axial Tensors for *trans*-Cyclopropane-*1,2*-d_2, $C_3H_4D_2$ (**6**)[a-c]

			$P^\lambda_{\alpha,\beta}$						$M^\lambda_{\alpha\beta}$	
λ	α	β		FPC/APT[d]	FPC/MPA[e]	$M^\lambda_{\alpha\beta}$	$(M^\lambda_{\alpha\beta})^\lambda$	$(i/4\hbar c)L^\lambda_{\alpha\beta}$	FPC/APT[d]	FPC/MPA[e]
C_2	X	X	−0.103	0.039	−0.523	0.000	0.000	0.000	0.000	0.000
	X	Y	−0.160	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	X	Z	0.000	0.000	0.000	0.083	0.047	0.036	0.008	−0.108
	Y	X	−0.160	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Y	Y	0.082	0.039	−0.523	0.000	0.000	0.000	0.000	0.000
	Y	Z	0.000	0.000	0.000	−0.144	−0.081	−0.063	−0.014	0.187
	Z	X	0.000	0.000	0.000	0.029	0.057	−0.028	−0.008	0.108
	Z	Y	0.000	0.000	0.000	−0.050	−0.099	0.049	0.014	−0.187
	Z	Z	0.137	0.039	−0.523	0.000	0.000	0.000	0.000	0.000
D_7	X	X	−0.031	−0.019	0.261	−0.020	−0.033	0.014	0.000	0.000
	X	Y	−0.062	0.000	0.000	0.149	0.139	0.010	−0.008	0.114
	X	Z	0.039	0.000	0.000	0.054	0.028	0.026	−0.007	0.089
	Y	X	−0.062	0.000	0.000	−0.126	−0.101	−0.026	0.008	−0.114
	Y	Y	0.041	−0.019	0.261	0.020	0.033	−0.014	0.000	0.000
	Y	Z	0.023	0.000	0.000	−0.094	−0.048	−0.046	0.011	−0.154
	Z	X	0.087	0.000	0.000	0.028	0.027	0.001	0.007	−0.089
	Z	Y	0.050	0.000	0.000	−0.049	−0.046	−0.003	−0.011	0.154
	Z	Z	−0.068	−0.019	0.261	0.000	0.000	0.000	0.000	0.000

[a] Cartesian geometry (in atomic units): C_1(0.000000, 1.651825, 0.000000), C_2(−1.430523, −0.825913, 0.000000), C_3(1.430523, −0.825913, 0.000000), H_4(0.000000, 2.727768, −1.738702), H_5(0.000000, 2.727768, 1.738702), H_6(−2.362315, −1.363884, −1.738702), D_7(−2.362315, −1.363884, 1.738702), D_8(2.362315, −1.363884, −1.738702), and H_9(2.362315, −1.363884, 1.738702). Origin is center of mass of C_3H_6. Geometry is experimental geometry of C_3H_6 of J. L. Duncan and G. R. Burns [*J. Mol. Spectrosc.* **1969**, *30*, 253]:[17] $r_{CC} = 1.514$ Å, $r_{CH} = 1.082$ Å, $\theta_{HCH} = 116.50°$, and $\theta_{HCC} = 117.11°$. [b] All ab initio calculations using the 6-31G(ext) basis set.[17] [c] Notation and units as in Table I. Origin for all atomic axial tensors is center of mass of C_3H_6. [d] $q_{C_2} = 0.039$ and $q_{D_7} = -0.019$ au. [e] $q_{C_2} = -0.523$ and $q_{D_7} = 0.261$ au.

FPC and CO equations render the predictions of these equations substantially indeterminate.

These conclusions are based on large basis set calculations for eight relatively small molecules. It is theoretically possible that calculations of greater accuracy and/or for a wider variety of molecules might modify our conclusions. However, this appears unlikely. While the quantitative significance of electron correlation in calculations of rotational strengths has not yet been explored, there is no obvious reason why it should be the dominant contributor thereto. We have documented very thoroughly the accuracy, relative to the Hartree–Fock limit, of the results used in the present paper via studies both of sum rules for atomic polar and axial tensors and of the gauge dependence of rotational strengths.[10,17,18] The probability that the results will change appreciably on approaching the Hartree–Fock limit more closely is negligible. In the case of **7** we have also documented the accuracy of the $P^\lambda_{\alpha\beta}$ and $M^\lambda_{\alpha\beta}$ tensors given in Table VII via quantitative comparison of predictions of absorption and VCD spectra[11] and of the paramagnetic susceptibility tensor of oxirane[43]

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(43) Stephens, P. J.; Jalkanen, K. J.; Lazzeretti, P.; Zanasi, R. *Chem. Phys. Lett.* **1989**, *156*, 509.

Table VII. Atomic Polar and Axial Tensors for *trans*-Oxirane-*2,3-d*$_2$, $C_2H_2D_2O$ (7)[a–c]

			$\mathbf{P}^{\lambda}_{\alpha\beta}$						$\mathbf{M}^{\lambda}_{\alpha\beta}$	
λ	α	β		FPC/APT[d]	FPC/MPA[e]	$\mathbf{M}^{\lambda}_{\alpha\beta}$	$(\mathbf{M}^{\lambda}_{\alpha\beta})^{\lambda}$	$(i/4\hbar c)\mathbf{L}^{\lambda}_{\alpha\beta}$	FPC/APT[d]	FPC/MPA[e]
O_1	X	X	−0.440	−0.639	−0.832	0.000	0.000	0.000	0.000	0.000
	X	Y	0.000	0.000	0.000	−0.722	−0.556	−0.166	−0.241	−0.314
	X	Z	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Y	X	0.000	0.000	0.000	0.242	0.089	0.153	0.241	0.314
	Y	Y	−0.404	−0.639	−0.832	0.000	0.000	0.000	0.000	0.000
	Y	Z	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	X	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Y	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Z	−1.072	−0.639	−0.832	0.000	0.000	0.000	0.000	0.000
C_2	X	X	0.368	0.349	−0.029	0.000	0.000	0.000	0.000	0.000
	X	Y	0.000	0.000	0.000	0.104	0.179	−0.074	−0.070	0.006
	X	Z	0.000	0.000	0.000	0.049	−0.079	0.127	0.120	−0.011
	Y	X	0.000	0.000	0.000	−0.077	−0.126	0.049	0.070	−0.006
	Y	Y	0.262	0.349	−0.029	0.000	0.000	0.000	0.000	0.000
	Y	Z	0.011	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	X	0.000	0.000	0.000	−0.348	−0.229	−0.118	−0.120	0.011
	Z	Y	0.127	0.000	0.000	0.000	0.000	0.000	0.000	0.000
	Z	Z	0.417	0.349	−0.029	0.000	0.000	0.000	0.000	0.000
D_4	X	X	−0.074	−0.015	0.223	−0.014	−0.015	0.001	0.000	0.000
	X	Y	−0.090	0.000	0.000	0.071	0.069	0.002	0.004	−0.067
	X	Z	−0.046	0.000	0.000	−0.035	−0.031	−0.005	−0.009	0.132
	Y	X	−0.042	0.000	0.000	0.032	0.006	0.026	−0.004	0.067
	Y	Y	−0.030	−0.015	0.223	0.007	0.020	−0.013	0.000	0.000
	Y	Z	−0.059	0.000	0.000	−0.121	−0.110	−0.012	0.006	−0.097
	Z	X	0.003	0.000	0.000	−0.046	0.000	−0.046	0.009	−0.132
	Z	Y	−0.036	0.000	0.000	0.016	−0.009	0.025	−0.006	0.097
	Z	Z	0.060	−0.015	0.223	0.013	−0.005	0.018	0.000	0.000

[a] Cartesian geometry (in atomic units): O_1(0.000000, 0.000000, 1.512211), C_2(0.000000, −1.381390, −0.805940), C_3(0.000000, 1.381390, −0.805940), D_4(−1.748934, −2.379468, −1.201879), H_5(1.748934, −2.379468, −1.201879), H_6(−1.748934, 2.379468, −1.201879), and D_7(1.748934, 2.379468, −1.201879). Origin is center of mass of C_2H_4O. Geometry is experimental geometry of C. Hirose [*Bull. Chem. Soc. Jpn.* **1974**, *47*, 1311]:[18] $r_{CC} = 1.462$ Å, $r_{CO} = 1.428$ Å, $r_{CH} = 1.086$ Å, $\theta_{HCH} = 116.905°$, $\theta_{COC} = 61.582°$, $\theta_{HCO} = 114.50°$, and $\theta_{HCC} = 119.10°$. [b] All ab initio calculations with the 6-31G(ext) basis set.[18] [c] Notation and units as in Table I. Origin for all atomic axial tensors is center of mass of C_2H_4O. [d] $q_O = -0.639$, $q_C = 0.349$, and $q_H = -0.015$ au. [e] $q_O = -0.832$, $q_C = -0.029$, and $q_H = 0.223$ au.

to experimental data. In the case of **6**, predictions have also been compared to VCD spectra.[17] Unfortunately only qualitative comparison has been made so far since rotational strengths have not been extracted from the (gas phase) VCD spectra.[48]

The range of molecules studied is limited to relatively small, neutral molecules containing C, N, O, F, and H. It is theoretically possible that for molecules of larger size, for ions, and for molecules involving a wider range of elements the results could be different. In particular, one might argue that the magnitude of the "$\vec{P}\cdot\vec{L}$" terms should increase with increasing molecular size since $(\vec{P}^{\lambda}_{i}\cdot\vec{R}_{\lambda'\lambda} \times \vec{P}^{\lambda'}_{i})$ increases linearly with $\mathbf{R}_{\lambda'\lambda}$. However, the vectors $\vec{P}^{\lambda}_{i}$ and $\vec{P}^{\lambda'}_{i}$ depend respectively on $\mathbf{S}_{\lambda\alpha,i}$ and $\mathbf{S}_{\lambda'\alpha,i}$, which quantitate the *simultaneous* involvement of nuclei λ and λ′ in the *i*th vibrational mode. As $\vec{R}_{\lambda'\lambda}$ increases, the coupling of the motion of nuclei λ and λ′ will generally diminish. Consequently, $(\vec{P}^{\lambda}_{i}\cdot\vec{R}_{\lambda'\lambda} \times \vec{P}^{\lambda'}_{i})$ is not a simple linear function of $\vec{R}_{\lambda'\lambda}$, and the "$\vec{P}\cdot\vec{L}$" terms are not in general a predictable function of molecular size. An exception to this occurs when the motions of λ and λ′ are interrelated by symmetry. For example, assume that only λ and λ′ contribute to the *i*th mode and that a C_2 axis exists. Consider the in-phase symmetrical motion of λ and λ′. Symmetry requires that

$$C_2\vec{P}^{\lambda}_{i} = \vec{P}^{\lambda'}_{i} \qquad (19)$$

independently of the magnitude of $\vec{R}_{\lambda'\lambda}$. In this case $(\vec{P}^{\lambda}_{i}\cdot\vec{R}_{\lambda'\lambda} \times \vec{P}^{\lambda'}_{i}$ does increase linearly with $|R_{\lambda'\lambda}|$. However, the in-phase vibration is always accompanied by an out-of-phase mode, for which

$$C_2\vec{P}^{\lambda}_{i} = -\vec{P}^{\lambda'}_{i} \qquad (20)$$

leading to a value of $(\vec{P}^{\lambda}_{i}\cdot\vec{R}_{\lambda'\lambda} \times \vec{P}^{\lambda'}_{i})$ of equal magnitude but opposite in sign to that for the in-phase mode. The net VCD arising from these two modes depends not only on their rotational strengths but also on their splitting and their line widths. As $|R_{\lambda'\lambda}|$ increases, the splitting will diminish and become much less than the line width. The net VCD is then reduced in magnitude, relative to that of one of the transitions, in the ratio of the splitting to the line width. In this case, the continual increase in rotational strength of the two transitions with increasing $|R_{\lambda'\lambda}|$ is compensated by a simultaneous decrease in splitting.

The conclusion that the "$\vec{P}\cdot\vec{M}$" terms of eq 1 are not negligible is not particularly surprising since there is no obvious convincing reason why the opposite should be the case. In one sense it is disappointing. Our earlier calculations have shown that with conventional basis sets $(M^{\lambda}_{\alpha\beta})^{DO}$ tensors are calculated less accurately than $\mathbf{P}^{\lambda}_{\alpha\beta}$ tensors.[15,17] The accuracy of rotational strength calculations for a given basis set is thus greater when the "$\vec{P}\cdot\vec{L}$" terms are dominant and, vice versa, worse when the "$\vec{P}\cdot\vec{M}$" terms are dominant. The general dominance of the "$\vec{P}\cdot\vec{M}$" terms in our calculations implies that rotational strengths are calculated less accurately than dipole strengths, for a given choice of basis set. Basis sets, giving improved performance in $(\mathbf{M}^{\lambda}_{\alpha\beta})^{DO}$ tensor calculations, are clearly required to diminish this differential in accuracy.

The derivation of the APT, FPC, and CO equations by systematic approximations to Stephens' equation, together with the quantitative study of the accuracy of these equations, provides for the first time a clear perspective of their content, interrelationships, and accuracy. The earlier derivations of these equations[24–27] were unrelated, proceeding from entirely different premises. All involved from the beginning extremely drastic approximations of questionable validity. It was thus impossible to define the relationship and relative accuracy of these equations to each other or to any equations derived rigorously by systematic approximations to the exact general equation for rotational strengths.

To be more specific, the APT equation was derived in two ways. Initially[24] it was obtained as an approximation to the localized molecular orbital (LMO) equation of Nafie and Walnut.[44] The latter was derived via two fundamental approximations: (1) that the *i*th electron is localized on a specific atom, so that

$$\vec{r}_i = \vec{r}_{i0,0} + \Delta\vec{r}_i \qquad (21)$$

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(44) Nafie, L. A.; Walnut, T. H. *Chem. Phys. Lett.* **1977**, *49*, 441.

where $\vec{r}_{i0,0}$ is its centroid of position, and (2) the orbital angular momentum of the ith electron is approximated by

$$\vec{r}_i \times \vec{p}_i = \vec{r}_{i0,0} \times \vec{p}_i \tag{22}$$

The second of these approximations discards electronic angular momentum about the electronic centroid $\vec{r}_{i0,0}$. In deriving the APT equation,[24] Freedman and Nafie further arbitrarily approximated $\vec{r}_{i0,0}$ by $\vec{R}_\lambda^0$, where λ is the nucleus at which the ith electron is localized.

In the subsequent derivation of the APT equation[25] Freedman and Nafie started from an assumption that the molecular electric dipole moment is the sum of atomic components

$$\vec{\mu}_{\text{el}}^{\text{G}} = \sum_\lambda \vec{\mu}_\lambda^{\text{G}} \tag{23}$$

and postulated a rotational strength expression

$$R(0\rightarrow 1)_i = \hbar/4c\left\{\sum_\lambda \frac{\partial \vec{\mu}_\lambda^{\text{G}}}{\partial Q_i}\right\}\cdot\left\{\sum_\lambda \vec{R}_\lambda^0 \times \frac{\partial \vec{\mu}_\lambda^{\text{G}}}{\partial Q_i}\right\} \tag{24}$$

Subsequent approximations led to an equation of the form of the APT equation. Although somewhat different in detail, the second derivation maintains the assumption of the first that electronic angular momentum about $\vec{R}_\lambda^0$ can be neglected.

The FPC equation is due initially to Schellman,[26] although it was implicitly used earlier by Deutsche and Moscowitz.[45] It was derived very simply via the assumption that molecules are constituted of masses carrying partial charges, q_λ, and that

$$\vec{\mu}_{\text{el}} = \sum_\lambda q_\lambda \vec{R}_\lambda \qquad \vec{\mu}_{\text{mag}} = \sum_\lambda \left(\frac{q_\lambda}{2M_\lambda c}\right)(\vec{R}_\lambda \times \vec{P}_\lambda) \tag{25}$$

Electrons do not appear explicitly in this derivation.

The coupled oscillator equation was introduced into the theory of VCD by Holzwarth and Chabay.[27] The initial postulate is of two, equivalent systems containing a vibrational chromophore that interact weakly. Both the electric and magnetic dipole transition moments of the dimeric assembly are expressed in terms of monomeric electric dipole transition moments.

All of these derivations incorporate major approximations from the beginning. In the derivation of the APT equation via the LMO equation, the assumptions that electrons are localized and that $|\Delta\vec{r}_i| \ll |\vec{r}_{i0,0}|$ are very drastic. The alternative derivation starts from an equation postulated ad hoc and not derived from fundamental equations. The derivation of the FPC equation makes the obviously drastic approximation that a molecule can be regarded as a set of masses of fixed fractional charge. The derivation of the CO equation starts from the assumption of a weakly coupled dimer, a drastic approximation to a covalently bonded molecule.

It is now clear that the APT equation is the most general of the three (APT, FPC, and CO) equations. Although earlier derivations obtained approximations in which the atomic polar tensors were drastically approximated, we have shown that the equation can be derived in terms of exact atomic polar tensors. The accuracy of the APT equation is then limited only as a result of the neglect of the "$\vec{P}\cdot\vec{M}$" terms of eq 1. The FPC and CO equations are both approximations to the APT equation, different in nature. The FPC approximation simply (but drastically) approximates the atomic polar tensors. The CO approximation relies principally on the existence of a pair of normal modes whose normal coordinates are related by symmetry. It also presumes that the normal coordinates involve displacements of two groups of atoms whose distance apart is much greater than the interatomic distances within each group.

Most importantly, it is now clear exactly what is omitted by the APT equation in its most exact form, and thence also by the approximations to the exact APT equation, in the form of the FPC and CO equations. The "$\vec{P}\cdot\vec{M}$" term of eq 1 is present in none of the approximate equations, showing that these equations entirely omit physics fundamental to the description of vibrational rotational strengths. That a contribution of this general nature is omitted is not surprising since (implicitly or explicitly) the neglect of such a term is central to the earlier derivations of the APT, FPC, and CO equations. However, previous to our work, useful expressions for this contribution were not available and its magnitude could not be directly assessed.

In the absence of a more rigorous equation against which the accuracies of the APT, FPC, and CO equations could be calibrated, a number of attempts have been made to assess their validity by direct comparison to experimental VCD spectra. In the only application to date of the APT equation, the VCD of the C–H stretching modes of 3-methylcyclohexanone and of three isotopomers of alanine were computed with partial success.[24] Atomic polar tensors were calculated using CNDO theory.

The FPC equation has been utilized more widely. The earliest VCD spectra {of the C–H and C–D stretching modes of $C_6H_5CH(OH)CF_3$ and $(CH_3)_3CCHDCl$, respectively[46]} were compared to FPC calculations with some success.[28] However, the VCD spectrum of $C_6H_6CH(OH)CF_3$ was obtained using the neat liquid, and subsequent work found a quite different spectrum in dilute solution.[47] In addition, the dominant conformation of $C_6H_5CH(OH)CF_3$ is not known and for both $C_6H_5CH(OH)CF_3$ and $(CH_3)_3CCHDCl$ highly approximate force fields were used (in the former C_6H_5 and CF_3 groups were replaced by single effective masses). Further calculations[29] did not lead to greater success. Subsequently, FPC calculations were compared to the VCD of the C–H stretching modes of several molecules, using geometries and force fields generated using the consistent force field (CFF) methodology. The earliest study involved spirononadiene and was moderately successful with the exception of the ethylenic C–H stretching modes.[31] However, four conformations exist whose relative populations were unknown and individual transitions were not resolved. In predicting the VCD spectrum it was therefore necessary to sum the contributions of many overlapping transitions of four conformers, using estimated line shapes and relative populations. In varying degree these difficulties also exist in subsequent studies of 3-methylcyclohexanone[36] and a set of monoterpenes.[34] The uncertain significance of the comparison of theory to the VCD spectra of highly overlapping C–H stretching modes is underlined by two further studies using the FPC equation of 3-methylcyclohexanone,[33,35] using different valence force fields, both reportedly also finding good agreement between theory and experiment. The valence force fields and CFF used for 3-methylcyclohexanone[33,35,36] give different assignments of the C–H stretching spectrum; not all can be correct. FPC calculations have also been compared with the VCD of the C–H and C–D stretching modes in cyclohexanone-*2*-d_1 and *trans*-cyclohexanone-*2,6*-d_2[37] and of the C–H stretching modes in three isotopomers of alanine.[38] The agreement in both cases was poor. Recently, a thorough study of the accuracy of the FPC equation has been carried out by Keiderling and co-workers for *trans*-cyclobutane-*1,2*-d_2.[40,41] The VCD spectrum down to ~900 cm^{-1} was studied in both gas and solution phases. Force fields fit to extensive vibrational data for several isotopomers of cyclobutane were used. The structure of cyclobutane is known. Despite the existence of two *trans*-d_2 conformers, their relative populations are known. With carefully chosen partial charges, together with an optimum force field, good qualitative agreement was found between observed and predicted VCD spectra. However, it was necessary to use very different charges for the C–H and C–D stretching modes and for the

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[45] Deutsche, C. W.; Moscowitz, A. *J. Chem. Phys.* **1968**, *49*, 3257.

[46] Holzwarth, G.; Hsu, E. C.; Mosher, H. S.; Faulkner, T. R.; Moscowitz, A. *J. Am. Chem. Soc.* **1974**, *96*, 251.

[47] Nafie, L. A.; Keiderling, T. A.; Stephens, P. J. *J. Am. Chem. Soc.* **1976**, *98*, 2715.

[48] Cianciosi, S. J.; Spencer, K. M.; Freedman, T. B.; Nafie, L. A.; Baldwin, J. E. *J. Am. Chem. Soc.* **1989**, *111*, 1913.

[49] Note that in ref 4 this equation is incorrect and ∓ on the right-hand side should be replaced by ±.

[50] Note that this algorithm for atomic charges has been proposed and utilized independently by J. Cioslowski [*J. Am. Chem. Soc.* **1989**, *111*, 8333].

Table VIII. Atomic Polar and Axial Tensors for Oxaziridine, CH_2ONH (**8**)[a-c]

			$P^{\lambda}_{\alpha\beta}$						$M^{\lambda}_{\alpha\beta}$	
λ	α	β		FPC/APT[d]	FPC/MPA[e]	$M^{\lambda}_{\alpha\beta}$	$(M^{\lambda}_{\alpha\beta})^{\lambda}$	$(i/4\hbar c)L^{\lambda}_{\alpha\beta}$	FPC/APT[d]	FPC/MPA[e]
O_1	X	X	−0.401	−0.489	−0.729	0.109	0.117	−0.008	0.000	0.000
	X	Y	−0.031	0.000	0.000	0.111	0.024	0.087	0.170	0.254
	X	Z	−0.262	0.000	0.000	−0.042	−0.044	0.002	−0.005	−0.007
	Y	X	0.066	0.000	0.000	−0.542	−0.419	−0.123	−0.170	−0.254
	Y	Y	−0.351	−0.489	−0.729	−0.071	−0.064	−0.007	0.000	0.000
	Y	Z	0.079	0.000	0.000	0.440	0.369	0.071	0.099	0.147
	Z	X	−0.172	0.000	0.000	0.011	0.009	0.003	0.005	0.007
	Z	Y	−0.013	0.000	0.000	−0.208	−0.124	−0.085	−0.099	−0.147
	Z	Z	−0.716	−0.489	−0.729	−0.006	−0.007	0.001	0.000	0.000
C_2	X	X	0.459	0.498	0.169	−0.007	0.001	−0.008	0.000	0.000
	X	Y	0.023	0.000	0.000	0.386	0.234	0.153	0.168	0.057
	X	Z	−0.009	0.000	0.000	0.029	0.029	0.000	0.005	0.002
	Y	X	0.010	0.000	0.000	0.039	0.204	−0.165	−0.168	−0.057
	Y	Y	0.492	0.498	0.169	0.081	0.093	−0.012	0.000	0.000
	Y	Z	−0.077	0.000	0.000	−0.040	0.060	−0.099	−0.100	−0.034
	Z	X	−0.110	0.000	0.000	−0.017	−0.019	0.002	−0.005	−0.002
	Z	Y	−0.022	0.000	0.000	0.329	0.256	0.073	0.100	0.034
	Z	Z	0.543	0.498	0.169	−0.015	−0.019	0.003	0.000	0.000
N_3	X	X	−0.362	−0.170	−0.238	0.019	0.020	−0.002	0.000	0.000
	X	Y	−0.002	0.000	0.000	−0.274	−0.190	−0.083	−0.005	−0.007
	X	Z	0.175	0.000	0.000	0.091	0.095	−0.004	−0.002	−0.002
	Y	X	−0.047	0.000	0.000	0.113	0.110	0.003	0.005	0.007
	Y	Y	−0.110	−0.170	−0.238	0.009	0.010	−0.001	0.000	0.000
	Y	Z	−0.002	0.000	0.000	−0.449	−0.403	−0.046	−0.070	−0.098
	Z	X	0.191	0.000	0.000	0.093	0.093	0.000	0.002	0.002
	Z	Y	0.022	0.000	0.000	0.052	0.030	0.021	0.070	0.098
	Z	Z	−0.038	−0.170	−0.238	−0.058	−0.069	0.011	0.000	0.000
H_4	X	X	0.059	0.010	0.258	0.050	0.061	−0.011	0.000	0.000
	X	Y	−0.013	0.000	0.000	0.033	−0.013	0.046	0.006	0.144
	X	Z	0.041	0.000	0.000	0.026	−0.004	0.030	0.005	0.115
	Y	X	−0.040	0.000	0.000	0.042	0.055	−0.014	−0.006	−0.144
	Y	Y	−0.030	0.010	0.258	−0.002	−0.003	0.001	0.000	0.000
	Y	Z	0.069	0.000	0.000	0.016	0.024	−0.008	−0.003	−0.086
	Z	X	0.061	0.000	0.000	−0.036	−0.025	−0.011	−0.005	−0.115
	Z	Y	0.018	0.000	0.000	0.004	−0.030	0.035	0.003	0.086
	Z	Z	0.003	0.010	0.258	−0.044	−0.065	0.021	0.000	0.000
H_5	X	X	0.031	−0.003	0.236	−0.066	−0.089	0.023	0.000	0.000
	X	Y	0.018	0.000	0.000	0.010	−0.036	0.046	−0.002	0.131
	X	Z	0.078	0.000	0.000	−0.039	−0.020	−0.020	0.001	−0.098
	Y	X	0.051	0.000	0.000	0.059	0.061	−0.002	0.002	−0.131
	Y	Y	−0.051	−0.003	0.236	0.005	0.004	0.001	0.000	0.000
	Y	Z	−0.073	0.000	0.000	0.028	0.030	−0.002	0.001	−0.088
	Z	X	0.055	0.000	0.000	0.032	0.020	0.012	−0.001	0.098
	Z	Y	−0.015	0.000	0.000	0.009	−0.025	0.034	−0.001	0.088
	Z	Z	0.009	−0.003	0.236	0.050	0.067	−0.017	0.000	0.000
H_6	X	X	0.214	0.155	0.303	−0.099	−0.089	−0.010	0.000	0.000
	X	Y	0.005	0.000	0.000	−0.017	−0.026	0.008	−0.003	−0.006
	X	Z	−0.022	0.000	0.000	−0.208	−0.117	−0.091	−0.068	−0.132
	Y	X	−0.040	0.000	0.000	0.034	0.031	0.003	0.003	0.006
	Y	Y	0.051	0.155	0.303	−0.021	−0.020	−0.001	0.000	0.000
	Y	Z	0.004	0.000	0.000	−0.022	−0.069	0.047	0.089	0.175
	Z	X	−0.024	0.000	0.000	0.064	−0.023	0.087	0.068	0.132
	Z	Y	0.009	0.000	0.000	−0.155	−0.041	−0.114	−0.089	−0.175
	Z	Z	0.198	0.155	0.303	0.067	0.051	0.016	0.000	0.000

[a] Cartesian geometry (in atomic units): O_1(−0.807133, −0.039072, −1.391701), C_2(−0.807133, −0.039072, 1.346901), N_3(1.650604, −0.039072, 0.122350), H_4(−1.328711, −1.778867, 2.224956), H_5(−1.491107, 1.659150, 2.208604), and H_6(2.305941, 1.747914, −0.083550). Origin is center of mass of CH_2ONH. Geometry is 3-21G SCF geometry:[17] $r_{C_2O_1} = 1.449$ Å, $r_{C_2N_3} = 1.453$ Å, $r_{O_1N_3} = 1.528$ Å, $r_{C_2H_4} = 1.068$ Å, $r_{C_2H_5} = 1.071$ Å, $r_{N_3H_6} = 1.013$ Å, $\theta_{C_2O_1N_3} = 58.365°$, $\theta_{O_1C_2H_4} = 115.80°$, $\theta_{N_3C_2H_4} = 115.18°$, $\theta_{O_1C_2H_5} = 115.21°$, $\theta_{N_3C_2H_5} = 119.50°$, $\theta_{H_6N_3O_1} = 103.59°$, $\theta_{H_6N_3C_2} = 110.75°$, $\theta_{H_4C_2H_5} = 116.81°$, $\tau_{O_1C_2N_3H_6} = -93.457°$, and $\tau_{H_5C_2N_3H_6} = 11.90°$. [b] All ab initio calculations using the 6-31G(ext) basis set.[17] [c] Notation and units as in Table I. Origin for all atomic axial tensors is center of mass of CH_2ONH. [d] $q_{O_1} = -0.489$, $q_{C_2} = 0.498$, $q_{N_3} = -0.170$, $q_{H_4} = 0.010$, $q_{H_5} = -0.003$, $q_{H_6} = 0.155$ au. [e] $q_{O_1} = -0.729$, $q_{C_2} = 0.169$, $q_{N_3} = -0.238$, $q_{H_4} = 0.258$, $q_{H_5} = 0.236$, $q_{H_6} = 0.303$ au.

mid-IR spectral region to generate this agreement. A single set of charges throughout leads to grossly inaccurate results in one or the other region.

The results obtained using the FPC equation thus vary greatly in both success and credibility. In addition, in all cases, no matter how accurate or inaccurate the geometry and force field employed may be, the results are intrinsically ambiguous, since they are a function of the fixed partial charges for whose choice no uniquely defined protocol exists.

The CO equation has been employed in a very small number of cases, since VCD spectra possessing the characteristic bisignate feature predicted by this equation have been observed infrequently. "Coupled oscillator VCD spectra" were first observed in the O–H stretching modes of dimethyl tartrate[30] and were compared to the predictions of the CO equation. Subsequently, this work was extended to the C=O stretching modes.[32] Observed VCD spectra were in reasonable agreement with predictions for some possible structures of dimethyl tartrate and inconsistent with other possible structures. Since at this time the actual structure remains unknown, this work obviously does not serve to test the accuracy of the CO equation. The C=O stretching VCD spectra of several steroids containing two C=O groups have also been compared to the CO equation.[39] None of the molecules studied possessed C_2 (or higher) symmetry and equivalent carbonyl groups. The

Table IX. Dipole and Rotational Strengths for NHDT (**1**)[a,b]

	D			*R*				
ν (cm^{-1})	*c*	FPC/APT[d]	FPC/MPA[e]	*f*	"$\vec{P}\cdot\vec{M}$"[g]	"$\vec{P}\cdot\vec{L}$"[h]	FPC/APT[i]	FPC/MPA[j]
3562	4.1	32.1	67.6	0.2	0.2	0.1	0.1	0.3
2601	4.6	27.4	57.6	-1.2	-0.8	-0.4	-0.6	-1.4
2176	5.0	21.8	45.9	1.2	0.7	0.5	0.7	1.5
1484	64.7	65.4	137.7	-5.1	-3.5	-1.6	-1.1	-2.4
1195	35.1	38.2	80.4	9.9	7.0	2.9	1.9	4.0
827	518.1	227.3	478.3	-4.9	-3.6	-1.4	-0.9	-1.9

[a] *D* and *R* in 10^{-40} esu^2 cm^2 and 10^{-44} esu^2 cm^2, respectively. [b] Frequencies and normal coordinates from the harmonic force field of J. L. Duncan and I. M. Mills [*Spectrochim. Acta* **1964**, *20*, 523]. [c] Calculated using ab initio $P^{\lambda}_{\alpha\beta}$ tensors. [d] Calculated using FPC/APT $P^{\lambda}_{\alpha\beta}$ tensors. [e] Calculated using FPC/MPA $P^{\lambda}_{\alpha\beta}$ tensors. [f] Calculated using ab initio $M^{\lambda}_{\alpha\beta}$ tensors. [g] "$\vec{P}\cdot\vec{M}$" contribution. [h] "$\vec{P}\cdot\vec{L}$" contribution. [i] "$\vec{P}\cdot\vec{L}$" contribution calculated using FPC/APT $P^{\lambda}_{\alpha\beta}$ tensors. [j] "$\vec{P}\cdot\vec{L}$" contribution calculated using FPC/MPA $P^{\lambda}_{\alpha\beta}$ tensors.

Table X. Dipole and Rotational Strengths for Hydrazine, NH_2NH_2 (**2**)[a,b]

	D			*R*							
ν (cm^{-1})		FPC/APT	FPC/MPA		"$\vec{P}\cdot\vec{M}$"	"$\vec{P}\cdot\vec{L}$"	FPC/APT	FPC/MPA	CO[c,d]	CO[c,e]	CO[e,f]
3766	11.2	42.1	105.6	24.6	40.7	-16.1	-25.3	-65.9	-8.8	-12.2	-12.9 (-)
3759	9.6	23.4	63.9	-27.4	-42.0	14.6	26.0	68.3	8.8	12.2	12.9 (+)
3643	0.3	8.2	25.9	-0.7	-0.4	-0.3	-4.5	-11.6	-0.2	-0.5	-0.3 (+)
3629	1.8	11.3	30.2	5.2	5.3	-0.1	3.5	8.4	0.2	0.5	0.3 (-)
1871	24.2	15.8	38.1	3.3	13.2	-9.9	1.7	1.7			
1848	32.0	110.9	303.0	-7.7	-21.8	14.1	-2.4	-4.6			
1398	10.5	1.1	3.4	-48.9	-35.0	-14.0	5.6	16.2			
1387	15.9	8.5	15.7	47.2	31.7	15.6	-8.2	-20.9			
1174	45.9	21.7	57.7	-22.2	1.4	-23.6	-5.3	-14.0			
936	705.6	220.1	587.3	220.4	77.8	142.5	39.5	102.9			
797	495.8	145.4	380.3	-197.3	-67.4	-129.9	-32.1	-84.1			
489	198.5	61.5	138.4	54.2	23.0	31.2	8.7	23.6			

[a] Notation and units as in Table IX. [b] Frequencies and normal coordinates from 3-21G SCF force field.[17] [c] Calculated using eq 14. (+) and (-) designate the symmetric and antisymmetric modes, respectively. [d] $\vec{R}^0_{BA} = \vec{R}_{N_2N_1}$. [e] $\vec{R}^0_{BA} = \vec{R}_{H_4H_3}$ for 3766- and 3759-cm^{-1} bands and $\vec{R}_{H_6H_5}$ for 3643- and 3629-cm^{-1} bands. [f] $\vec{R}^0_{BA} = \vec{R}_{H_4H_3}\cdot\hat{e}_{N_2N_1})$ or $(\vec{R}_{H_6H_5}\cdot\hat{e}_{N_2N_1})\hat{e}_{N_2N_1}$, where $\hat{e}_{N_2N_1}$ is the unit vector along $\vec{R}_{N_2N_1}$.

Table XI. Dipole and Rotational Strengths for Propane-*1,1,1-d*$_3$-*2-d*$_1$, CH_3CHDCD_3 (**3**)[a,b]

	D			*R*				
ν (cm^{-1})		FPC/APT	FPC/MPA		"$\vec{P}\cdot\vec{M}$"	"$\vec{P}\cdot\vec{L}$"	FPC/APT	FPC/MPA
3253	91.1	7.0	196.3	-15.6	-12.7	-2.9	-1.1	-19.9
3249	62.5	4.4	158.5	19.8	10.9	8.9	1.1	24.0
3216	25.5	3.7	23.5	-5.3	0.8	-6.1	-0.1	-3.9
3191	45.0	1.1	43.1	1.0	1.3	-0.3	0.0	-0.5
2408	47.3	4.3	146.7	-5.1	-3.3	-1.8	-0.4	-8.5
2406	42.3	3.6	149.4	6.4	2.7	3.7	0.5	10.0
2365	30.1	4.6	34.9	-1.5	-0.1	-1.4	0.0	-1.0
2290	30.7	1.1	46.2	0.3	0.4	-0.1	0.0	-0.1
1673	6.7	4.7	176.6	-1.9	-1.5	-0.4	0.1	-3.5
1672	13.0	4.8	150.3	2.2	2.0	0.2	-0.1	2.4
1573	3.0	15.7	574.5	0.2	0.2	0.0	0.0	-0.2
1491	2.5	13.4	146.5	4.4	4.0	0.4	1.4	27.3
1470	7.7	13.4	110.6	-0.7	-0.5	-0.1	-1.8	-32.6
1271	6.0	4.2	163.5	-16.2	-15.1	-1.1	-1.9	-72.3
1248	3.0	8.0	365.7	4.0	3.2	0.8	2.6	79.4
1213	0.5	2.3	104.8	-1.2	-0.7	-0.5	-0.3	-15.7
1207	6.7	2.7	133.5	-0.5	-0.6	0.0	0.1	5.2
1204	10.0	4.2	150.7	2.5	1.6	0.9	0.7	25.9
1151	3.7	6.0	134.3	9.1	9.1	0.0	-0.4	-2.5
998	1.0	1.9	40.0	-0.3	-0.1	-0.2	0.2	-1.5
912	1.3	8.2	211.1	-2.1	-1.8	-0.3	-1.3	-29.1
852	0.7	4.1	71.3	-0.5	-0.5	0.0	0.1	-1.6
804	2.4	5.1	117.3	1.3	0.9	0.5	0.8	21.7
668	5.4	23.2	478.7	-0.1	0.0	-0.1	-0.1	-3.4
366	0.2	7.3	103.8	0.0	0.0	0.0	0.0	0.1
265	0.0	0.8	0.0	0.0	0.0	0.0	0.0	0.0
186	0.0	0.1	0.1	0.0	0.0	0.0	0.0	0.0

[a] Notation and units as in Table IX. [b] Frequencies and normal coordinates from 3-21G SCF force field.[17]

use of the CO equation thus involved the further assumption that the inequivalence of the C=O groups and the lowering of symmetry below C_2 does not affect the applicability of the CO equation. The agreement between theory and experiment was mixed, in some cases excellent, in others poor. Most recently, the CO equation has been applied to a band of a bis-alaninato complex of Co(III),[42] assigned to C-C alanine stretching modes. Agreement of theory and experiment was good.

The application of the CO equation generally requires two major assumptions: (1) the directions of the electric dipole transition moments of the individual groups that are coupled together and (2) the sign and magnitude of the splitting of the symmetric and antisymmetric vibrational modes. All applications to date have involved stretching vibrational modes of (to a first approximation)

Table XII. Dipole and Rotational Strengths for Fluorohydroxylamine, NHF(OH) (4)[a,b]

	D			*R*				
ν (cm^{-1})		FPC/APT	FPC/MPA		“$\vec{P}\cdot\vec{M}$”	“$\vec{P}\cdot\vec{L}$”	FPC/APT	FPC/MPA
3854	106.1	111.9	180.6	−16.1	−16.9	0.8	0.9	2.3
3637	18.6	15.5	68.5	6.7	7.9	−1.2	−1.2	−3.1
1645	7.8	26.4	35.8	−8.9	−1.5	−7.4	−30.7	−68.6
1497	74.4	159.7	347.0	80.5	38.9	41.6	67.7	146.9
1228	348.9	243.7	563.0	−79.2	−35.5	−43.7	−49.9	−100.9
1095	739.6	198.4	201.9	−3.9	1.1	−4.9	3.1	2.2
1062	126.1	110.6	74.1	−10.6	−10.1	−0.5	2.2	0.8
521	193.2	266.3	342.4	12.0	8.7	3.3	6.8	9.0
394	1103.2	767.1	1271.3	24.3	3.3	21.0	28.6	46.2

[a] Notation and units as in Table IX. [b] Frequencies and normal coordinates from 3-21G SCF force field.[17]

Table XIII. Dipole and Rotational Strengths for Carbodiimide, HN=C=NH (5)[a,b]

	D			*R*							
ν (cm^{-1})		FPC/APT	FPC/MPA		“$\vec{P}\cdot\vec{M}$”	“$\vec{P}\cdot\vec{L}$”	FPC/APT	FPC/MPA	CO[c,d]	CO[c,e]	CO[c,f]
3819	33.2	83.9	51.7	−50.7	−14.8	−36.0	−130.5	−78.8	−57.3	−15.0	−88.3 (+)
3815	405.9	312.5	174.0	49.4	10.6	38.8	136.7	82.1	57.3	15.0	88.3 (−)
2425	1821.8	261.3	0.9	−3.4	3.6	−7.0	1.1	0.6			
1400	0.0	0.3	0.1	−0.3	−0.1	−0.2	1.1	0.5			
831	152.6	1119.7	190.7	−178.2	−61.1	−117.1	−392.9	−124.6			
823	3180.8	1918.6	588.2	215.4	66.4	149.0	393.2	137.8			
781	704.0	1287.5	587.5	337.2	7.1	330.1	471.0	244.6			
579	1049.8	641.2	314.9	−12.2	4.0	−16.2	−91.5	19.3			
563	33.3	106.3	119.0	−40.9	−18.4	−22.5	51.2	−41.7			

[a] Notation and units as in Table IX. [b] Frequencies and normal coordinates from 3-21G SCF force field.[17] [c] Calculated using eq 14. (+) and (−) designate the symmetric and antisymmetric modes, respectively. [d] $\vec{R}^0_{BA} = \vec{R}_{NN}$. [e] $\vec{R}^0_{BA} = \vec{R}_{HH}$. [f] $\vec{R}^0_{BA} = (\vec{R}_{HH}\cdot\hat{e}_{NN})\hat{e}_{NN}$, where $\hat{e}_{NN}$ is the unit vector along $\vec{R}_{NN}$.

Table XIV. Dipole and Rotational Strengths for *trans*-Cyclopropane-*1,2*-d_2, $C_3H_4D_2$ (6)[a,b,g]

	D			*R*							
ν (cm^{-1})		FPC/APT	FPC/MPA		“$\vec{P}\cdot\vec{M}$”	“$\vec{P}\cdot\vec{L}$”	FPC/APT	FPC/MPA	CO[c,d]	CO[c,e]	CO[c,f]
3105	31.3	1.3	242.9	12.8	12.0	0.8	0.1	14.0			
3075	1.9	0.0	3.4	14.3	13.5	0.8	0.1	17.7			
3073	28.9	0.6	109.7	−41.5	−38.9	−2.6	−0.3	−47.6			
3041	36.1	0.3	62.1	14.6	13.6	0.9	0.1	16.8			
2271	5.3	0.1	12.7	−10.1	−9.1	−1.0	−0.1	−23.9	−4.2	−1.0	−7.0 (+)
2260	27.3	0.8	137.8	9.6	8.6	1.0	0.1	23.6	4.2	1.0	7.0 (−)
1459	0.6	1.4	246.2	0.5	0.4	0.0	0.1	11.3			
1345	1.0	1.1	208.1	−4.5	−4.4	−0.2	−0.5	−82.4			
1300	2.9	2.4	436.9	6.5	6.3	0.2	0.6	104.4			
1188	0.1	0.0	1.0	1.9	1.8	0.1	0.0	7.9			
1138	3.4	0.6	112.3	−19.3	−17.9	−1.4	−0.7	−133.2			
1094	6.5	0.9	154.9	−4.1	−3.2	−0.9	−0.1	−14.2			
1055	8.9	1.1	199.8	22.6	19.5	3.0	0.5	89.9			
1049	13.9	2.2	406.9	−4.6	−4.7	0.1	−0.1	−23.9			
955	0.2	1.7	305.2	0.9	1.0	−0.1	0.4	70.2			
907	32.7	0.8	147.7	3.8	5.3	−1.5	−0.1	−11.8			
862	106.9	0.5	84.8	3.4	6.7	−3.2	0.1	13.4			
785	77.6	1.2	214.5	−9.5	−13.9	4.5	−0.1	−19.4			
735	10.5	1.9	336.7	3.2	2.3	0.9	−0.1	−18.6			
633	4.1	0.3	54.0	−1.5	1.1	−2.6	0.0	8.1			
619	0.9	0.3	53.6	0.8	−0.2	1.1	0.0	−2.5			

[a] Notation and units as in Table IX. [b] Frequencies and normal coordinates from the harmonic force field of J. L. Duncan and G. R. Burns [*J. Mol. Spectrosc.* **1969**, *30*, 253].[17] [c] Calculated using eq 14. (+) and (−) designate the symmetric and antisymmetric modes, respectively. [d] $\vec{R}^0_{BA} = \vec{R}_{C_1C_2}$. [e] $\vec{R}^0_{BA} = \vec{R}_{DD}$. [f] $\vec{R}^0_{BA} = (\vec{R}_{DD}\cdot\hat{e}_{C_1C_2})\hat{e}_{C_1C_2}$, where $\hat{e}_{C_1C_2}$ is the unit vector along $\vec{R}_{C_1C_2}$. [g] For comparison of absorption and VCD spectra predicted from *D* and *R* values to experimental data see ref 17.

diatomic nature, and transition moments have been assumed to be along the relevant diatomic bond directions. In all cases, symmetric–antisymmetric mode splittings have been calculated assuming their origin to be in electric dipole–dipole interactions (eq 16). Since without a more detailed vibrational analysis the accuracy of these assumptions cannot be assessed, the significance of the predictions of the CO equation is correspondingly uncertain.

Despite the considerable optimism regarding the utility of the APT, FPC, and CO equations expressed in the literature it is clear that so far, as a result of comparison to experimental data, *general* validity has not been established for any of these equations. Our calculations, presented above, lead to the expectation that such general validity will not be found by a larger number of substantially more definitive studies.

Subsequent to the completion of this work, a similar study, comparing the predictions of the APT, FPC, and localized molecular orbital (LMO) equations for 1,3-dideuterioallene to those of the a priori theory, has been carried out.[19] The conclusions of this latter study support and confirm those arrived at above.

Conclusion

The APT, FPC, and CO equations for vibrational rotational strengths result from Stephens' equation when specific approximations are made to the atomic polar and axial tensors, $\mathbf{P}^{\lambda}_{\alpha\beta}$ and $\mathbf{M}^{\lambda}_{\alpha\beta}$. The results presented here show that *in general* these approximations are of poor accuracy. It is our conclusion therefore

Table XV. Dipole and Rotational Strengths for *trans*-Oxirane-2,3-d_2, $C_2H_2D_2O$ (7)[a,b,g]

	D			R							
ν (cm^{-1})		FPC/APT	FPC/MPA		"$\vec{P}\cdot\vec{M}$"	"$\vec{P}\cdot\vec{L}$"	FPC/APT	FPC/MPA	CO[c,d]	CO[c,e]	CO[c,f]
3042	56.5	4.7	116.8	30.7	26.0	4.8	0.4	13.6	11.6	6.6	19.9 (−)
3037	8.9	0.1	3.8	−26.7	−22.0	−4.7	−0.5	−13.2	−11.6	−6.6	−19.9 (+)
2238	10.6	0.5	2.6	14.4	10.1	4.3	0.9	6.0	7.8	2.1	13.5 (+)
2225	51.1	7.5	62.1	−14.8	−11.2	−3.7	−0.5	−8.1	−7.8	−2.1	−13.5 (−)
1402	14.8	11.0	2.6	−10.0	−10.2	0.2	1.4	6.4			
1327	1.9	7.3	228.6	−2.2	−2.6	0.3	0.2	−59.6			
1227	32.6	5.8	174.2	13.6	17.1	−3.5	−1.8	56.7			
1131	1.0	36.4	165.3	4.3	3.7	0.6	−4.4	−44.0			
1115	10.9	36.4	49.8	9.3	1.1	8.2	−3.2	56.8			
963	129.8	68.5	39.7	−40.8	−46.0	5.2	9.0	−22.0			
914	24.2	43.3	3.3	−1.0	3.7	−4.8	4.5	−2.4			
875	162.9	44.6	65.5	5.8	20.6	−14.8	−4.4	14.7			
813	60.9	92.1	164.9	1.3	0.3	1.0	−1.0	5.5			
751	156.8	13.6	299.5	15.0	7.3	7.7	−0.2	−4.6			
648	1.2	2.4	144.5	0.7	0.3	0.4	0.4	−3.2			

[a] Notation and units as in Table IX. [b] Frequencies and normal coordinates from a 6-31G(ext) SCF (SQM) force field.[11,18] [c] Calculated using eq 14. (+) and (−) designate the symmetric and antisymmetric modes, respectively. [d] $\vec{R}^0_{BA} = \vec{R}_{CC}$. [e] $\vec{R}^0_{BA} = \vec{R}_{HH}$ or $\vec{R}_{DD}$. [f] $\vec{R}^0_{BA} = (\vec{R}_{HH}\cdot\hat{e}_{CC})\hat{e}_{CC}$ or $(\vec{R}_{DD}\cdot\hat{e}_{CC})\hat{e}_{CC}$, where $\hat{e}_{CC}$ is the unit vector along $\vec{R}_{CC}$. [g] For comparison of absorption and VCD spectra predicted from *D* and *R* values to experimental data see ref 11.

Table XVI. Dipole and Rotational Strengths for Oxaziridine, CH_2ONH (**8**)[a,b]

	D			R				
ν (cm^{-1})		FPC/APT	FPC/MPA		"$\vec{P}\cdot\vec{M}$"	"$\vec{P}\cdot\vec{L}$"	FPC/APT	FPC/MPA
3606	7.0	26.7	111.3	4.5	5.1	−0.6	0.0	−0.8
3434	14.0	3.0	68.7	0.9	0.9	0.0	−0.1	2.2
3324	30.7	1.3	30.6	−1.9	−1.4	−0.5	0.0	−0.3
1689	2.2	3.4	164.0	−1.5	−1.4	0.0	−0.2	6.0
1436	70.5	39.0	146.4	−35.9	−34.6	−1.3	1.1	−35.7
1354	83.0	43.9	378.2	−8.1	−1.6	−6.5	−15.6	81.2
1314	3.6	37.7	61.3	−3.6	4.1	−7.7	−1.5	−13.5
1265	130.8	64.6	137.5	23.1	11.3	11.8	8.2	28.7
1155	21.2	23.1	49.2	6.7	−5.5	12.2	7.9	−18.1
1062	77.1	26.1	170.7	2.4	13.8	−11.4	−0.7	−59.4
879	44.3	62.9	117.7	−2.6	−1.8	−0.8	0.1	3.3
823	236.4	106.8	175.5	−5.5	−6.6	1.1	−3.0	−5.7

[a] Notation and units as in Table IX. [b] Frequencies and normal coordinates from 3-21G SCF force field.[17]

Table XVII. Coupled Oscillator Splittings

$(\omega_+ - \omega_-)$[a]	$\Delta\omega$[b]	$\Delta\omega$[c]	$\Delta\omega$[d]	θ[e]	mode
Hydrazine					
−7	−0.15	−0.21	−0.05		N−H
14	−0.52	−0.11	−0.14		N−H
Carbodiimide					
4	−26.4	−6.8	−7.2	23.9	N−H
trans-2,3-Dideuteriooxirane					
−5	−10.0	−1.8	−2.0	16.0	C−H
13	−10.2	−1.6	−2.0	22.6	C−D
trans-1,2-Dideuteriocyclopropane					
11	−5.0	−0.8	−1.2	21.6	C−D

[a] Splitting (cm^{-1}) from force field calculation. [b] Splitting (cm^{-1}) from eq 16; $\vec{R}^0_{BA}$ defined in Tables X and XIII−XV, in footnote *d*. [c] Splitting (cm^{-1}) from eq 16; $\vec{R}^0_{BA}$ defined in Tables X and XIII−XV, in footnote *e*. [d] Splitting (cm^{-1}) from eq 16; $\vec{R}^0_{BA}$ defined in Tables X and XIII−XV, in footnote *f*. [e] Angle between the transition moment and the bond direction for the oscillator.

that these approximate equations do not provide a sound basis for the prediction and analysis of VCD spectra. Past applications of these equations should be reexamined. Future application appears to be unwarranted.

More generally, our results illustrate the dangers inherent in all heuristic theories of vibrational rotational strengths. A variety of other equations of similar ilk to the APT, FPC, and CO equations have also been put forth.[1,2] The accuracy of these equations has yet to be demonstrated.

At the present time the application of Stephens' theory at the ab initio SCF level of approximation is limited to relatively small molecules. Theoretical methodologies with lower computational requirements, applicable to larger molecules, should obviously continue to be sought. In our opinion, these should be obtained by systematic, well-defined approximations to the rigorous equation now available and tested carefully against the rigorous theory to define their utility.

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Note Added in Proof. Subsequent to completion of this paper Chernovitz, Freedman, and Nafie [*Biopolymers* **1987**, *26*, 1879], Lee, Roberts, and Diem [*Biopolymers* **1989**, *28*, 1759], and Shaw, Ibrahim, and Wieser [*J. Phys. Chem.* **1990**, *94*, 125] have reported applications of the APT, FPC, and/or CO equations for rotational strengths. Dutler and Rauk (*J. Am. Chem. Soc.* **1989**, *111*, 6957) have also criticized the APT equation.